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Carbenoid reactions of trifluoromethylelement compounds. Part 2 ☆. The reactions of bis(trifluoromethyl)cadmium complexes with cyclic ethers and thioethers. A ^{113}Cd NMR and ^{19}F NMR study of the intermediates

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Abstract

The reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ with tetrahydrofuran (THF), tetrahydrothiophene and tetrahydrothiopyran in the presence of $BF_3 \cdot CH_3CN$ yield open-chain difluoromethyl ethers and thioethers. The final product from the reaction with tetrahydrothiophene, [4-(difluoromethylthio)butyl]tetrahydrothiophenium tetrafluoroborate, has been fully characterized, whereas the products of the reactions with THF yielded polymeric ethers containing the OCF_2H group. All cadmium-containing intermediates formed during the reaction with tetrahydrothiophene could be detected by ^{113}Cd and ^{19}F NMR spectroscopy indicating that a carbenoid mechanism is more likely than a 'free' difluorocarbene mechanism. In contrast to the reactions of the trifluoromethylcadmium derivative with THF in the presence of BF_3, reactions in the presence of BCl_3 or $InCl_3$ yielded 4-chlorobutyl(difluoromethyl) ether.

Keywords: Difluoromethyl ether; Difluoromethyl thioethers; NMR spectroscopy; Mass spectrometry; Mechanism

1. Introduction

While $Cd(CF_3)_2$ complexes have been shown to be useful reagents in the synthesis of organometallic [2] and organic [3] compounds containing a CF_3 group, less is known about the potential of these derivatives as sources of difluorocarbene or difluorocarbenoids. $Cd(CF_3)_2$ and $Zn(CF_3)_2$ complexes are known to eliminate difluorocarbene at elevated temperature [4] or in the presence of arsenic trihalides [5] and tungsten fluorides [6]; carbene reactions at very low temperatures have also been reported [7].

In some previous papers, we have reported spectroscopic evidence for the formation of difluoromethyl ethers during the reactions of $Cd(CF_3)_2$ complexes with $Fe(CO)_4X_2$ [8] or Main Group III halides [9], but a definite identification of the products could not be made. The first hint for carbenoid reactions of $Cd(CF_3)_2$ complexes was found in our attempts to obtain bis- and tris-(trifluoromethyl)iodine(III) compounds [10]. $Cd(CF_3)(CF_2OCOCF_3)$ could be detected by ^{113}Cd and ^{19}F NMR spectroscopy as an intermediate in the reactions of $I(CF_3)(OCOCF_3)_2$ with $Cd(CF_3)_2$ complexes in the presence of $B(OCOCF_3)_3$. This intermediate is a unique species which only has congeners in difluorocarbene transition metal complexes [11].

These results encouraged us to study carbenoid reactions of trifluoromethyl-cadmium and -zinc derivatives intensively. In a recent paper, we described the successful synthesis of alkyl(difluoromethyl)chalcogen compounds by BF_3-assisted reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ or $ZnBr(CF_3) \cdot 2CH_3CN$ with dialkylchalcogen compounds [1]. Herein we report the cleavage of cyclic ethers and thioethers, and present a proposal for the reaction mechanism on the basis of ^{113}Cd and ^{19}F NMR studies.

2. Results and discussion

2.1. Reaction of $Cd(CF_3)_2 \cdot 2CH_3CN$ with THF in the presence of BF_3 adducts

The reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ in the presence of $BF_3 \cdot O(CH_3)_2$ in neat THF gave a mixture of gelatinous orange products. In the ^{19}F NMR spectrum of the mixture

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☆ For Part 1, see Ref. [1].

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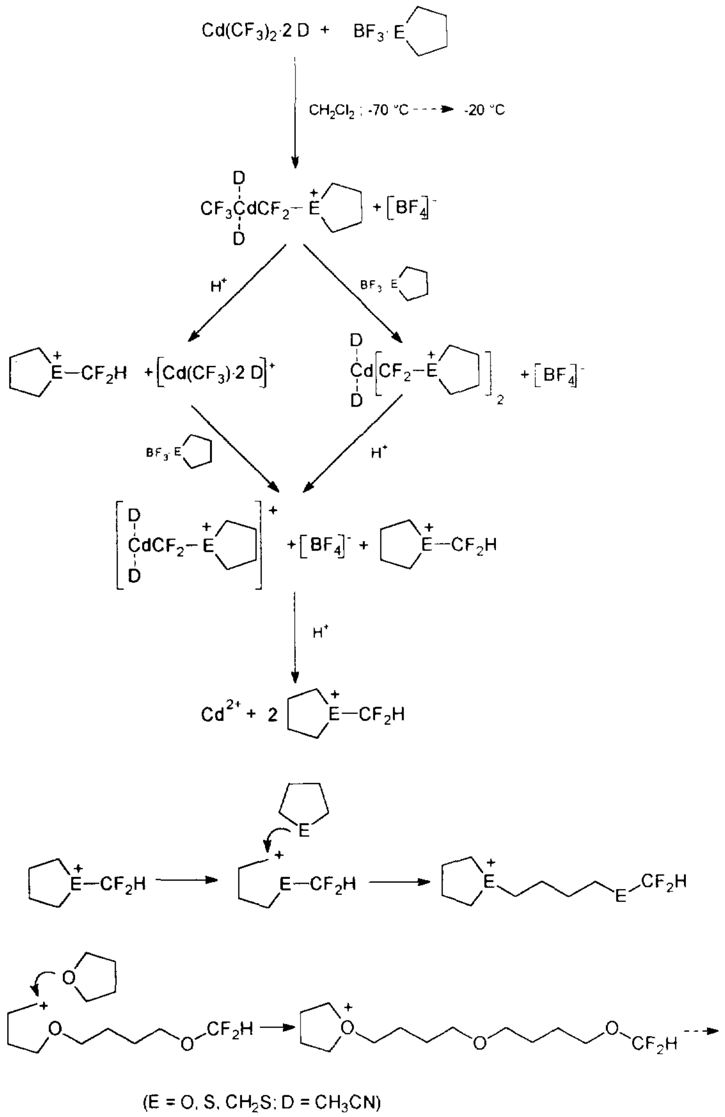


Scheme 1. Proposed mechanism of the formation of open-chain difluoromethyl ethers and thioethers from cyclic ethers or thioethers.

diluted with CCl_4, the dominating resonance of one difluoromethyl ether ($\delta = -84.0$ ppm, $^2J(^{19}F-^1H) = 75.7 \pm 0.5$ Hz) could be detected besides the resonances of $Cd(CF_3)_2$ complexes, the solvent-stabilized $[Cd(CF_3)]^+$ cation, CF_3H and several BF_3 adducts. No spectroscopic evidence was found for tetrafluoroethylene or cyclohexafluoropropane, the oligomers of 'free' difluorocarbene. These results may be compared with those obtained from reactions of $Cu(CF_3)$ with $Cu(C_6F_5)$ or of $Cd(C_6F_5)X$ with $Cd(CF_3)X$ or $Zn(CF_3)X$ in the presence of CuBr [12]. These reactions only yielded $Cu(CF_2CF_2C_6F_5)$ even in the presence of alkenes, indicating a carbenoid reaction sequence.

All attempts to isolate the difluoromethyl ether from the reaction mixture failed. After distilling off all volatile components in vacuo on raising the temperature from 0 °C up to 40 °C, a glassy residue remained containing the CF_2H ether, traces of unreacted $Cd(CF_3)_2 \cdot 2THF$ and $[Cd(CF_3)]^+[BF_4]^-$, and BF_3 adducts. Washing the residue with various solvents did not allow a separation or purification of the difluoromethyl ether. The difluoromethyl ether itself decomposed in vacuo at temperatures above 40 °C leaving a yellow–brown oil. The ^{19}F NMR spectrum of the residue dissolved in cyclohexane gave evidence for a monofluoroethyl-group-containing product [$\delta = -218.54$ ppm, $^2J(^{19}F-^1H) = 48$ Hz, $^3J(^{19}F-^1H) = 23$ Hz]. In the distillate, formyl fluoride could be detected as a doublet at $\delta = +46.58$ ppm [$^2J(^{19}F-^1H) = 184$ Hz] [13]. This result indicates a complex reaction sequence including a cationic polymerization of the initially formed difluoromethyl ether as shown in Scheme 1.

In the first step an exchange of the complex ligand at the BF_3 molecule (CH_3CN or $(CH_3)_2O$ versus THF) occurs [14]. This exchange has also been studied by ^1H NMR spectroscopy in dilute $CDCl_3$ solution. As soon as excess THF was added to a solution of $BF_3 \cdot CH_3CN$, the resonances of THF ($\delta = 3.24$ and 1.38 ppm/$CDCl_3$) were shifted downfield ($\delta = 3.70$ and 1.81 ppm); the resonance of CH_3CN ($BF_3 \cdot CH_3CN$: $\delta = 1.99$ ppm) was shifted upfield ($\delta = 1.96$ ppm) indicating a fast ligand exchange. This conjugated

Table 1
Difluoromethyl ethers obtained from the deuteration experiments [a]

Reactants	Products obtained	
	with THF	with THF-d_8
$BF_3 \cdot CH_3CN$ + $Cd(CF_3)_2 \cdot 2CH_3CN$	$ROCF_2H$	$ROCF_2H$
$BF_3 \cdot CH_3CN$ + $Cd(CF_3)_2 \cdot 2CD_3CN$	$ROCF_2H$	$ROCF_2H$
$BF_3 \cdot CD_3CN$ + $Cd(CF_3)_2 \cdot 2CH_3CN$	$ROCF_2H$ $ROCF_2D$ (traces)	$ROCF_2H$ $ROCF_2D$ (100:6) [b]
$BF_3 \cdot CD_3CN$ + $Cd(CF_3)_2 \cdot 2CD_3CN$	$ROCF_2H$ (traces)	– $ROCF_2H$ [c] $ROCF_2D$ (100:37) [b]

[a] Molar ratio $Cd(CF_3)_2 \cdot 2D/BF_3 \cdot D \approx 2:1$, where $D = CH_3CN$ or CD_3CN.
[b] Ratio determined by integrating the ^{19}F NMR resonances.
[c] Molar ratio $Cd(CF_3)_2 \cdot 2D/BF_3 \cdot D \approx 2:3$.

acid–base couple now attacked the CF_3 group bound to the metal centre in a similar manner as also postulated in Ref. [8]. The cadmium–carbon bond of the first-formed oxonium ion was cleaved by one proton to give the *O*-(difluoromethyl)tetrahydrofuranium cation. Through the agency of this intermediate, cleavage of further THF rings in a kind of a cationic polymerization can take place to finally yield polyethers of the general formula $HCF_2O(CH_2)_4[O(CH_2)_4]_n$. From these results, a question arises regarding the source of the proton which cleaves the cadmium–carbon bond to yield the difluoromethyl group.

To achieve a definite result about the origin of the proton, all possible proton sources were successively replaced by their deuterated analogues. The results of these experiments are summarized in Table 1.

From the data obtained it is obvious that acetonitrile is the source of the proton. However, a decision as to whether the proton is abstracted from CH_3CN coordinated at BF_3, $Cd(CF_3)_2$, $[Cd(CF_3)]^+$ or the 'free' CH_3CN (produced during the equilibrium mentioned above), or an intermediately formed nitrilium salt [15] cannot be taken.

To explain the great amount of the CF_2H-group-containing difluoromethyl ether, it should be noted that the deuterated substrates used had a purity of 99 atom% deuterium, and that the specific conductivity of CH_3CN used in these reactions was 26-times the value for CD_3CN (CH_3CN: 6.85 μS cm^{-1}; CD_3CN: 0.26 μS cm^{-1}). Hence, a proton abstraction from partly deuterated acetonitrile molecules such as CHD_2CN or CH_2DCN, according to

$$CHD_2CN \longrightarrow H^+ + CD_2CN^- \qquad (1)$$

for example, should be considerably faster than deuterium abstraction.

The reactions also exclude THF or an open-chain cationic intermediate derived from THF as shown in Scheme 1 as the source of the proton. If this had been so, reactions in THF-d_8 should have provided evidence for the CF_2D-group-containing ether.

2.2. Reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ with THF in the presence of BCl_3 or $InCl_3$

Reactions in the presence of BCl_3 proceeded selectively with the formation of a single difluoromethyl ether; neither a change in colour nor a significant increase in viscosity as observed during the reactions with BF_3 occurred. In addition to the resonance of the difluoromethyl ether, only the resonances of $[BF_4]^-$ and $BF_3 \cdot THF$ could be detected in the ^{19}F NMR spectra. The same product together with small amounts of diethylene glycolmethyl(difluoromethyl) ether was obtained when $InCl_3$ was used instead of BCl_3 and $Cd(CF_3)_2 \cdot$diglyme was used instead of $Cd(CF_3)_2 \cdot 2CH_3CN$. However, polar CF_3-group-transfer reactions to give $In(CF_3)_{3-n}Cl_n$ ($n = 0$–2) occurred as parallel reactions [9]. After distilling off excess THF under reduced pressure, the difluoromethyl ether could be isolated by high-vacuum condensation as a colourless oil and was identified as (4-chlorobutyl) (difluoromethyl) ether, $Cl(CH_2)_4OCF_2H$. In this reaction, the source of the proton was one methoxy group of a diglyme molecule as described in Ref. [1].

Although a reaction sequence analogous to that shown in Scheme 1 seems to be the most probable, it cannot be excluded that an ether cleavage as described for $AlCl_3 \cdot THF$ in excess THF [16] to give $Cl_2AlO(CH_2)_4Cl$ may be the primary step. Intermediates of the type $Cl_2EO(CH_2)_4Cl$ ($E = B$, In) may also undergo similar exchange reactions.

The fact that an attack of CF_2 on the oxygen atom of ethers in reactions of 'free' difluorocarbene generated by different methods is not mentioned [17], supports our proposal of a carbenoid reaction.

2.3. Reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ with tetrahydrothiophene and tetrahydrothiopyran in the presence of $BF_3 \cdot CH_3CN$

The reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ with tetrahydrothiophene proceeded in a similar manner as described for reactions with THF. The advantage of this reaction is that many of the postulated intermediates formulated in the reaction sequence involving THF may be identified from the NMR spectra. In dichloromethane solution, the reaction commenced with an exchange between the acetonitrile molecules coordinated to the cadmium centre and tetrahydrothiophene. This exchange could be monitored by the change of the $^2J(^{111/113}Cd–^{19}F)$ coupling constants [$Cd(CF_3)_2 \cdot 2CH_3CN$: $^2J(^{111/113}Cd–^{19}F) = 446/466$ Hz [18]; $Cd(CF_3)_2 \cdot 2C_4H_8S$: $^2J(^{111/113}Cd–^{19}F) = 400/418$ Hz]. The resonances of the $Cd(CF_3)$ groups were located at ca. $\delta = -33$ ppm, with those of the $Cd(CF_2)$ groups at ca. $\delta = -77$ ppm. The resonances

Table 2
^{19}F NMR data for the reaction mixture $Cd(CF_3)_2 \cdot 2CH_3CN/BF_3 \cdot CH_3CN$/tetrahydrothiophene in CH_2Cl_2/CD_2Cl_2 at different temperatures (measurement temperature −70 °C; δ in ppm; $^2J(^{111/113}Cd–^{19}F)$ and $^2J(^{19}F–^1H)$ in Hz; $R^1 = CH_2CH_2CH_2CH_2S^+(CH_2)_4$; $R^2 = CH_2CH_2CH_2CH_2$)

	Temperature of reaction mixture (°C)					
	−70	−40	−20	−10	0	+21 [a]
$[Cd(CF_3)]^+$	−32.47	−32.65	−32.58	−32.58	−32.60	−32.64
	441/461	443/463	442/462	442/462	442/462	467/489
$Cd(CF_3)_2$	−33.07	−33.10	−33.09	−33.09	−33.08	−32.74
	400/418	400/418	399/418	400/418	399/418	397/417
$[Cd(CF_3)(CF_2SR^2)]^+$	−33.51	−33.60	−33.56	–	–	–
	425/445	426/445	427/445	–	–	–
$[Cd(CF_2SR^2)_2]^{2+}$	−76.59	−76.75	–	–	–	–
	≈194	≈193	–	–	–	–
$[Cd(CF_2SR^2)]^{2+}$	−76.99	−77.31	−77.03	–	–	–
	≈222	≈217	≈219	–	–	–
$[Cd(CF_3)(CF_2SR^2)]^+$	−77.14	−77.22	−77.21	–	–	–
	≈170	≈171	≈172	–	–	–
R^1-SCF_2H	–	–	–	–	−92.71	−92.58
	–	–	–	–	55.8	56.5
$[R^2$-$SCF_2H]^+$	−106.33	−106.31	−106.24	−106.24	−106.25	–
	53.2	53.2	53.2	53.2	53.2	–

[a] The ^{19}F NMR spectrum was recorded after stirring the mixture for 12 h at room temperature.

of the $Cd(CF_2)$ groups were broadened; hence, an exact determination of $^2J(^{111/113}Cd–^{19}F)$ could not be made. The doublet at $\delta = -105.8$ ppm [$^2J(^{19}F–^1H) = 53.4 \pm 0.5$ Hz; $^1J(^{19}F–^{13}C) = 292.2$ Hz] could be assigned to the *S*-(difluoromethyl)tetrahydrothiophenium cation; further resonances were those of two BF_3 adducts ($\delta = -143$ and -151 ppm) and $[BF_4]^-$ ($\delta = -150.5$ ppm). The exact chemical shifts and coupling constants are summarized in Table 2. Differences in chemical shifts may be due to concentration and temperature effects; differences in absolute values of the coupling constants to the same effects and additionally to the accuracy of the measurements (digital resolution, 1.387 Hz per pt.).

Assignment of the resonances to the cadmium-containing intermediates could be made from the signal splitting in the ^{113}Cd NMR spectrum as shown in Fig. 1 and by a comparison of the coupling constants. Four of the five intermediates detected in the ^{19}F NMR spectrum could be identified unambiguously in the corresponding ^{113}Cd NMR spectrum. The resonance of $Cd(CF_3)_2 \cdot 2C_4H_8S$ is centred at $\delta = -255.4$ ppm and split into a septet [$^2J(^{113}Cd–^{19}F) = 420 \pm 2$ Hz] due to the coupling of the cadmium nucleus with six fluorine atoms in two magnetically equivalent CF_3 groups. The resonance of $[Cd(CF_3)(CF_2SR^2)]^+$ is located at $\delta = -287.3$ ppm and split into a quadruplet (coupling with the CF_3 group) of triplets (coupling with the CF_2SR^2 group) with coupling constants $^2J(^{113}Cd–^{19}F) = 445 \pm 2$ Hz and $^2J(^{113}Cd–^{19}F) = 179 \pm 2$ Hz, respectively. The quadruplet at $\delta = -336.4$ ppm, $^2J(^{113}Cd–^{19}F) = 462 \pm 2$ Hz, is the resonance of a solvent-stabilized $[Cd(CF_3)]^+$ cation; the quintuplet at $\delta = -365.6$ ppm, $^2J(^{113}Cd–^{19}F) = 198 \pm 2$ Hz, caused by the coupling of the cadmium nucleus with two magnetically equivalent CF_2SR^2 groups, is the resonance of $[Cd(CF_2SR^2)_2]^{2+}$ dications. The broad signal ($\delta = -393$ ppm) might be assigned to $[Cd(CF_2SR^2)]^{2+}$; the signal at $\delta = -398$ ppm to solvated Cd^{2+} ions.

The detection of these intermediates emphasizes the formulation of the reaction sequence shown in Scheme 1.

From the data presented in Table 2, it is obvious that the cadmium-containing intermediates were only stable up to −20 °C. At −10 °C, only the stable cadmium species $Cd(CF_3)_2 \cdot 2C_4H_8S$ and $[Cd(CF_3)]^+$ could be detected in the ^{19}F NMR spectra among the resonances of the *S*-(difluoromethyl)thiophenium cation and the tetrafluoroborate anion. Raising the temperature from −20 °C to ambient temperature did not effect any change in relation to the chemical shifts or concentrations of the cadmium derivatives. An additional doublet was observed in the ^{19}F NMR spectrum centred at $\delta = -92.6$ ppm, $^2J(^{19}F–^1H) = 56.3$ Hz. The resonance of the *S*-(difluoromethyl)thiophenium cation disappeared as a function of time (stirring the reaction mixture at ambient temperature over a period of 12 h); in the same manner the new resonance at $\delta = -96.3$ ppm increased in intensity to become the only resonance of a difluoromethyl-group-containing derivative and was assigned to [4-(difluoromethylthio)butyl]tetrahydrothiophenium tetrafluoroborate. This derivative may be regarded as the condensation product of the initially formed *S*-(difluoromethyl)tetrathiophenium tetrafluoroborate with one molecule of tetrahydrothiophene.

A comparison of the NMR data of these cations with those of $[(C_2H_5)_2S(CF_2H)]^+$ and $(C_2H_5)S(CF_2H)$ [1] (Table 3) reveals that the CF_2H group in [4-(difluoromethylthio)butyl]tetrahydrothiophenium tetrafluoroborate is bonded to a sulphane and not to the sulphonium centre. The differences in character of the CF_2H groups is clearly demonstrated by the differences in the chemical shifts and the coupling constants in particular.

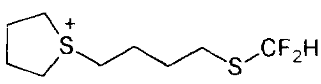
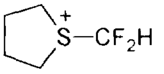
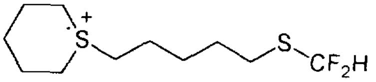
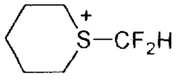
The same reaction sequence can also be applied to the reactions with tetrahydrothiopyran which finally yield [5-(difluoromethylthio)pentyl]tetrahydrothiopyranium tetrafluoroborate via the intermediacy of the *S*-(difluoromethyl)tetrahydrothiopyranium cation.

3. Experimental details

3.1. Materials

All commercially available compounds were purified by common methods [19]. Tetrahydrofuran, tetrahydrothiophene, tetrahydrothiopyrane and gaseous boron trifluoride were purchased from Aldrich Chemicals; BCl_3, $BF_3\cdot O(CH_3)_2$ and acetonitrile-d_3 (99% D atom) from Merck, Darmstadt (Germany); THF-d_8 (99% D atom) from Riedel-de Haën, Seelze (Germany) and $InCl_3$ from Heraeus, Karslruhe (Germany). $Cd(CF_3)_2\cdot 2CH_3CN$ and $Cd(CF_3)_2\cdot 2CD_3CN$ were prepared according to Ref. [18]. $BF_3\cdot CD_3CN$ was prepared by bubbling gaseous BF_3 into neat CD_3CN at 0 °C; the white solid was dried under reduced pressure to remove excess CD_3CN [20].

Table 3
^{19}F NMR data for difluoromethylsulphanes and difluoromethylsulphonium tetrafluoroborates [a]

	$C_2H_5SCF_2H$ [b]	$[(C_2H_5)_2SCF_2H]^+$ [b]
$\delta(CF_2H)$ [c]	-93.5	-104.4
$^2J(^{19}F-^1H)$	56.3	52.5
$^1J(^{19}F-^{13}C)$	271.1	291.0
		
$\delta(CF_2H)$ [c]	-93.1	-105.8
$^2J(^{19}F-^1H)$	56.3	53.4
$^1J(^{19}F-^{13}C)$	270.6	292.2
		
$\delta(CF_2H)$ [d]	-93.1	-106.4
$^2J(^{19}F-^1H)$	57.0	52.9
$^1J(^{19}F-^{13}C)$	270.8	293.0

[a] Resonance of $[BF_4]^-$ located at $\delta = -150 \pm 0.5$ ppm.
[b] Taken from Ref. [1].
[c] Solvent CH_2Cl_2.
[d] Solvent CH_3CN.

Nuclear magnetic resonance spectra were recorded on a Bruker FT NMR spectrometer AMX-300 (^{19}F, 282.4 MHz (CCl_3F, ext.); ^{113}Cd, 66.5 MHz [50 vol.% $(CH_3)_2Cd$ in $CDCl_3$, ext.]) and an AC-200 spectrometer (^{19}F, 188.3 MHz; ^1H, 200.1 MHz [$(CH_3)_4Si$, ext.]; $^{13}C\{^1H\}$, 50.3 MHz [$(CH_3)_4Si$, ext.]). Negative values indicate high-field shifts.

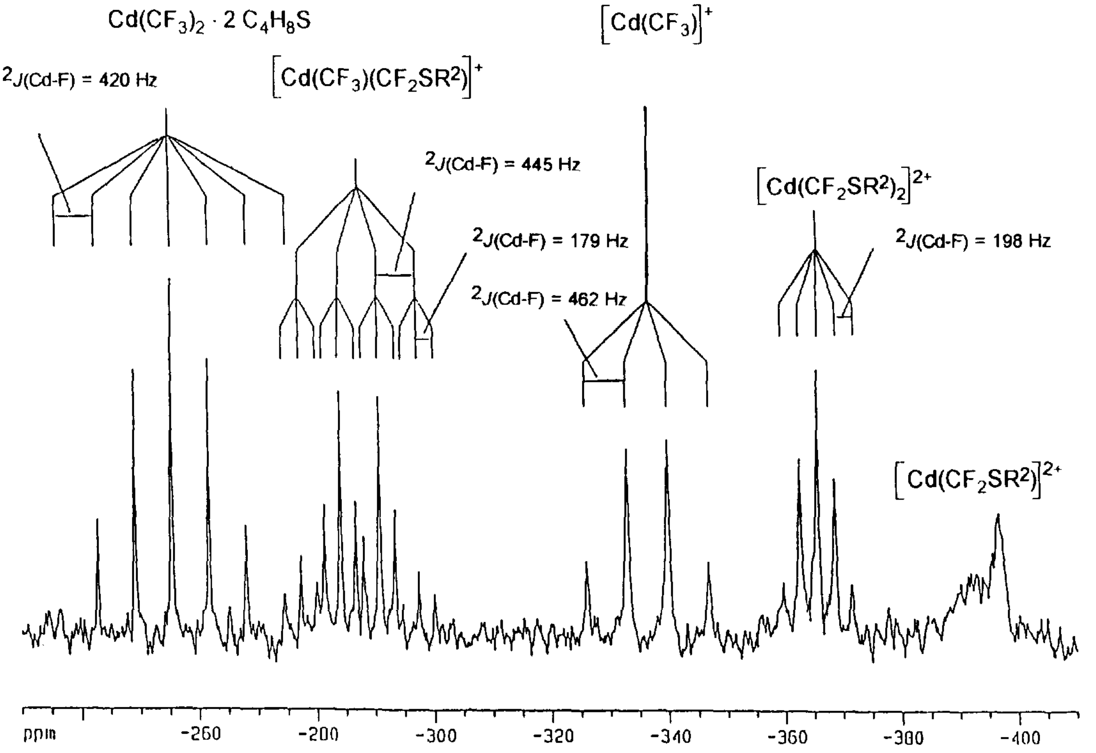


Fig. 1. ^{113}Cd NMR spectrum of the reaction mixture of $Cd(CF_3)_2\cdot 2CH_3CN$, tetrahydrothiophene and $BF_3\cdot CH_3CN$ in CH_2Cl_2 solution at −70 °C ($R^2 = CH_2CH_2CH_2CH_2$).

Carbon/hydrogen analysis was undertaken with a Heraeus CHN-O-RAPID analyzer, fluorine analysis after decomposition according to Ref. [21] and sulphur analysis gravimetrically after oxidation with elemental oxygen according to Ref. [22].

GC/MS couplings were carried out with the Varian spectrometer MATCH 7 (70 eV, evaporation in forevacuo).

3.2. General procedure

All reactions were carried out in a dry nitrogen atmosphere using Schlenk techniques. Carefully dried 25 ml round-bottom flasks equipped with a stop-cock were used as reaction vessels.

3.3. Reactions of $Cd(CF_3)_2 \cdot 2D$ ($D = CH_3CN$, CD_3CN) with THF and THF-d_8 in the presence of BF_3

$Cd(CF_3)_2 \cdot 2CH_3CN$ or $Cd(CF_3)_2 \cdot 2CD_3CN$ was dissolved in THF at −70 °C and the BF_3 adduct added to the solution. The molar ratio $Cd(CF_3)_2 \cdot 2CH_3CN/BF_3$ was ca. 2:1 in all cases. The reaction mixture was stirred for 2 h at this temperature and then slowly warmed up to room temperature. During the warming period the mixtures became more and more viscous and changed colour from colourless to orange. ^{19}F NMR spectra were recorded at different temperatures and indicated that the process of carbenoid reactions started at ca. −30 °C. On mixing the compounds at −20 °C or above, the carbenoid reaction only proceeded as a side-reaction; $[B(CF_3)F_3]^-$ could be detected as the major product ($\delta(CF_3) = -75.1$ ppm, $^2J(^{19}F-^{11}B) = 33.4$ Hz; $\delta(BF_3) = -155.2$ ppm, $^1J(^{19}F-^{11}B) = 39.3$ Hz [23]).

A typical procedure was as follows. To a solution consisting of 90 mg (0.27 mmol) of $Cd(CF_3)_2 \cdot 2CH_3CN$ in 2 ml of THF-d_8 at −70 °C was added $BF_3 \cdot CD_3CN$ (20 mg, 0.18 mmol). The reaction mixture was slowly warmed up to −30 °C and then stirred for 12 h at this temperature. The ^{19}F NMR spectrum recorded at −30 °C exhibited resonances corresponding to $[Cd(CF_3)]^+$ ($\delta = -33.5$ ppm, $^2J(^{111/113}Cd-^{19}F) = 504/527$ Hz), $Cd(CF_3)_2$ ($\delta = -34.4$ ppm, $^2J(^{111/113}Cd-^{19}F) = 444/464$ Hz), the difluoromethyl ether [$\delta = -83.1$ ppm (d, $^2J(^{19}F-^1H) = 75.7$ Hz)], the deuterodifluoromethyl ether [$\delta = -83.9$ ppm (t, $^2J(^{19}F-^2D) = 11.0$ Hz)] and $[BF_4]^-$ ($\delta = -151.6$ ppm). The CF_2HOR/CF_2DOR ratio was ca. 100:6.

3.4. Reactions of $Cd(CF_3)_2$ complexes with THF in the presence of $InCl_3$ or BCl_3

(a) With $InCl_3$

Solid $InCl_3$ (2.9 g, 13.11 mmol) was added at ambient temperature to a solution consisting of 7.6 g (19.76 mmol) of $Cd(CF_3)_2 \cdot$diglyme in 25 ml of THF. An exothermic reaction began, but within a few hours the reaction mixture became somewhat viscous and a white solid precipitated. The ^{19}F NMR spectrum of the reaction mixture recorded after a total reaction time of 48 h showed resonances corresponding to $Cd(CF_3)_2 \cdot 2THF$, $[Cd(CF_3)]^+$, $In(CF_3)_{3-n}Cl_n$ ($n = 0$, 1, 2) and two difluoromethyl ethers. The integrated ratio of $Cd(CF_3)$ compounds/$In(CF_3)$ compounds/difluoromethyl ethers was 71:45:100. All easily volatile components were distilled off in vacuo at ambient temperature. Raising the temperature to 50 °C allowed the separation of the two difluoromethyl ethers in a ratio of $CF_2HO(CH_2)_4Cl/CF_2HO[(CH_2)_2O]_2CH_3 = 12:1$. A further increase in temperature up to 100 °C caused the decomposition of the ethers. Only HF could be detected as the sole fluorine-containing decomposition product. The ethers could be identified by NMR spectroscopy and GC/MS coupling.

$CF_2HO(CH_2)_4Cl$: ^{19}F NMR (282.4 MHz, $CDCl_3$, 21 °C) δ: −84.4 [d, $^2J(^{19}F-^1H) = 75.2$ Hz, CF_2H] ppm. ^1H NMR (300.1 MHz, $CDCl_3$, 21 °C) δ: 6.12 [t, $^2J(^{19}F-^1H) = 75.2$ Hz, 1H, CF_2H]; 3.56 (m, 2H, OCH_2); 3.50 (m, 2H, CH_2Cl); 1.66 (m, 2H, CH_2); 1.55 (m, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 21 °C) δ: 116.1 [t, $^1J(^{19}F-^{13}C) = 260.1$ Hz, CF_2H]; 62.4 [t, $^3J(^{19}F-^{13}C) = 5.1$ Hz, OCH_2]; 45.0 (CH_2Cl); 29.5 (CH_2); 26.1 (CH_2) ppm. MS (GC-coupled) *m/z* (%) (70 eV, ions containing Cl refer to ^{35}Cl): 158 (4.0) [M^+]; 123 (22.4) [$M^+ - Cl$]; 81 (19.8) [$C_2H_3F_2O^+$]; 51 (10.1) [CHF_2^+].

$CF_2HO[(CH_2)_2O]_2CH_3$: ^{19}F NMR (282.4 MHz, $CDCl_3$, 21 °C) δ: −84.6 [d, $^2J(^{19}F-^1H) = 74.6$ Hz, CF_2H] ppm. MS (GC-coupled) *m/z* (%) (70 eV): 170 (10.1) [M^+]; 155 (5.4) [$M^+ - CH_3$]; 81 (100) [$C_2H_3F_2O^+$]; 51 (31.6) [CHF_2^+].

(b) With BCl_3

On to a frozen solution consisting of 310 mg (0.93 mmol) of $Cd(CF_3)_2 \cdot 2CH_3CN$ in 5 ml of THF were condensed 0.17 ml (1.95 mmol) of BCl_3. The solution was warmed to −40 °C under vigorous stirring. After 1 h, $Cd(CF_3)$ compounds could no longer be detected. The resonances in the ^{19}F NMR spectrum corresponded to $CF_2HO(CH_2)_4Cl$, $[BF_4]^-$ and a BF_3 adduct. $CF_2HO(CH_2)_4Cl$ was identified by its ^{19}F NMR spectrum after adding one drop of authentic material to the NMR sample. Distillative work-off (75 °C) caused decomposition of the ether.

3.5. Reactions of $Cd(CF_3)_2 \cdot 2CH_3CN$ with tetrahydrothiophene and tetrahydrothiopyran in the presence of $BF_3 \cdot CH_3CN$

(a) Reaction with tetrahydrothiophene

$Cd(CF_3)_2 \cdot 2CH_3CN$ (630 mg, 1.89 mmol) was dissolved in a mixture consisting of 4 ml of CH_2Cl_2 and 4 ml of CD_2Cl_2. The solution was cooled to −74 °C when $BF_3 \cdot CH_3CN$ (160 mg, 1.47 mmol) and tetrahydrothiophene (1.6 ml, 18.14 mmol) were added. The reaction mixture was stirred for 90 min at −70 °C. The NMR spectrum was measured at −70 °C. Then the reaction mixture was slowly warmed up to ambient temperature in steps of 10 °C, with an NMR sample being measured at −70 °C after every rise in temperature. The NMR data for the individual samples are summarized in

Table 2. All samples were collected after an overall reaction time of 12 h, when the solid residue was filtered off. All volatile substrates were distilled off at room temperature in vacuo. A red–brown waxy solid remained which contained about 2% of tetrahydrothiophene but was free of cadmium-containing compounds. From the ^{19}F, ^{1}H, ^{13}C{^{1}H} and DEPT NMR spectra, as well as elemental analysis, the novel compound could be identified as [4-(difluoromethylthio)butyl]tetrahydrothiophenium tetrafluoroborate.

[4-(Difluoromethylthio)butyl]tetrahydrothiophenium tetrafluoroborate: ^{19}F NMR (188.3 MHz, CD_2Cl_2, 20 °C) δ: -93.1 [d, $^{2}J(^{19}F-^{1}H) = 56.3$ Hz, $^{1}J(^{19}F-^{13}C) = 270.6$ Hz, 2F, CF_2H]; -150.9 [4F, $[BF_4]^-$] ppm. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C) δ: 6.92 [t, $^{2}J(^{19}F-^{1}H) = 56.4$ Hz, 1H, SCF_2H]; 3.52 (m, 2H, methylene chain); 3.38 (m, 2H, methylene chain); 3.17 (m, 2H, methylene chain); 2.83 (m, 2H, methylene chain); 2.30 (m, 4H, ring protons); 1.84 (m, 4H, ring protons) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2/CH_2Cl_2 (v/v = 1:1), 20 °C) δ: 121.6 [t, $^{1}J(^{19}F-^{13}C) = 271.7$ Hz, SCF_2H]; 43.3 [s, C-2,5 (ring)]; 41.6 [s, C-3,4 (ring)]; 28.6, 28.5 [s, C-2 and C-3 (chain)]; 26.4 [t, $^{3}J(^{19}F-^{13}C) = 3$ Hz, $CSCF_2H$]; 23.9 [s, C-1 (chain)] ppm. Elemental analysis for $C_9H_{17}BF_6S_2$ (314.16 g mol^{-1}): [Found (calculated)]: C, 34.53 (34.41); H, 5.72 (5.45); F, 35.48 (36.28); S, 18.89% (20.41%).

(b) Reaction with tetrahydrothiopyrane

$Cd(CF_3)_2 \cdot 2CH_3CN$ (160 mg, 0.48 mmol) was dissolved in 5 ml of CH_2Cl_2 at ambient temperature and 100 mg (0.92 mmol) of $BF_3 \cdot CH_3CN$ and 0.5 ml (4.82 mmol) of tetrahydrothiopyrane added to the solution at -72 °C. As soon as the resonance of the *S*-(difluoromethyl)tetrahydropyranium cation (for ^{19}F NMR data, see Table 3) could no longer be detected, the mixture was worked-up. All volatile substrates (CH_3CN, CHF_3, CH_2Cl_2 and tetrahydrothiopyrane) were distilled off in vacuo. The remaining residue was washed with $CHCl_3$. After evaporation of the chloroform, a yellow solid was obtained which was identified via its ^{19}F and ^{1}H NMR spectra to be [5-(difluoromethylthio)pentyl]-tetrahydrothiopyranium tetrafluoroborate.

[5-(Difluoromethylthio)pentyl]tetrahydrothiopyranium tetrafluoroborate: ^{19}F NMR (188.3 MHz, CH_2Cl_2, 21 °C) δ: -93.1 [d, $^{2}J(^{19}F-^{1}H) = 57.0$ Hz, $^{1}J(^{19}F-^{13}C) = 270.8$ Hz, 2F, CF_2H]; -150.7 [4F, $[BF_4]^-$] ppm. ^{1}H NMR (200.1 MHz, $CDCl_3$, 21 °C) δ: 6.82 [t, $^{2}J(^{19}F-^{1}H) = 56.5$ Hz, 1H, SCF_2H]; 3.66–3.10 (br m, 6H, methylene chain); 2.83 (4H, ring protons); 2.33–2.04 (br m, 4H, methylene chain); 1.82 (4H, ring protons); 1.59 (2H, ring protons) ppm.

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